Petroleum Coke: Summary of Composition and Evaluation of Inhalation Toxicity

Robert Sills, Toxics Unit Supervisor
MDEQ Air Quality Division
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This report briefly summarizes the available information relevant to the potential public health concern for inhalation exposure to petroleum coke from the storage piles located along the Detroit River waterfront. **The available information indicates that the storage piles do not pose a significant public health risk for inhalation exposure.**

According to AQD District staff, the petroleum coke is of the "green" form, i.e., not calcined. The storage piles were initiated in approximately November 2012. District staff also report that thus far, the storage piles have not been observed to generate more than a minimal amount of airborne dust. Generally speaking, petroleum coke is a less friable and dusty material than coal/coal dust. Minimal airborne dust may be equated to opacity levels that are less than 5% opacity, and that are below the National Ambient Air Quality Standards (NAAQS) for fine particulate matter (PM2.5), based on AQD's experience and policy (Mitchell, personal communication). The lowest PM2.5 NAAQS is 12 micrograms per cubic meter (ug/m^3).

The AQD operates ambient air monitors in the Detroit area for fine particulate matter (PM2.5). However, there are none that are positioned to adequately measure any impacts that the petroleum coke storage piles may have on the nearby ambient air PM2.5 levels. The nearest PM2.5 monitor is on W. Lafayette, approximately 1 mile NE of the storage piles. Review of the data from recent months does not indicate any unusual elevated PM2.5 levels with wind direction from the storage piles toward the monitors. PM2.5 levels have been below the NAAQS, and levels measured simultaneously at different monitoring stations have tracked similarly, although levels at the Dearborn monitor tend to be somewhat higher than at other monitoring stations (Fitzner, personal communication).

Based on the limited available information summarized above, there is no basis to suspect that the petroleum coke storage piles have posed a public health concern for locally elevated PM2.5 levels.

Besides the PM2.5 issue, consideration is also given to the particular toxicity that may be associated with fine particulates from petroleum coke or from the trace metal constituents of petroleum coke. There is no AQD Initial Threshold Screening Level (ITSL) for petroleum coke (green, or, calcined), and there is also no occupational exposure limit (OEL). The chemical constituents of petroleum coke and coal may be regarded as similar. Coal dust is exempt from the AQD's definition of Toxic Air Contaminants (TACs); it was on the list of 40 exempted substances when the AQD's air toxics rules were promulgated in 1992, presumably because it was recognized to have a low order of toxicity. Of course, coal dust can have toxic effects to the respiratory tract at relatively high levels of exposure, as may occur occupationally for example. The ACGIH has established a Threshold Limit Value – Time Weighted

Average (TLV-TWA) for coal dust at 0.4 mg/m^3 (anthracite) and 0.9 mg/m^3 (bituminous or lignite). These limits are set to protect workers from respiratory disease (pulmonary fibrosis; chronic bronchitis; emphysema; decreased pulmonary function). These coal dust occupational limits are about one order of magnitude lower than the occupational limits set for "generic" particulate: the OSHA Permissible Exposure Limits (PEL – TWA) for Particulates Not Otherwise Regulated are 15 mg/m^3 (total dust) and 5 mg/m^3 (respirable dust). The ACGIH Threshold Limit Values (TLV-TWA) for Particulates Not Otherwise Specified are 10 mg/m^3 (total dust) and 3 mg/m^3 (respirable dust). For dust from petroleum coke, which does not have specific occupational exposure limits, these limits may be useful as surrogate benchmarks. It is noted that these OELs are much higher than the PM2.5 NAAQS; this information is only offered to help lend perspective.

Neither petroleum coke dust nor coal dust are regulated as carcinogenic. Green coke was not carcinogenic in rats or monkeys exposed for two years by inhalation at up to 30 mg/m^3. Green coke was not genotoxic based on *in vivo* testing. Testing for reproductive or developmental effects in rats at up to 300 mg/m^3 for 35 days or longer did not induce such effects, and did not induce parental systemic toxicity. The chronic bioassays in rats and monkeys did find inflammatory and non-carcinogenic proliferative changes in rats, but not in monkeys. Systemic toxicity was not observed. The authors attributed these findings to non-specific responses of the respiratory tract to high concentrations of insoluble particles. Rats exposed to 50 mg/m^3 green coke (with a mass median aerodynamic diameter of 2.71 microns) for five days were found to have slight inflammatory responses in the lung (API, 2007; EPA, 2011).

Green petroleum coke (CAS #64741-79-3) exists as a solid substance composed of predominantly carbon in a polycrystalline porous matrix. Trace metals occur in petroleum coke, as metal chelates or porphyrins, or, intercalated in the coke structure and not chemically bonded (API, 2007). These forms would not be expected to become airborne, except as components of particulate matter. Various polyaromatic compounds have also been measured in petroleum coke samples (API, 2007).

Trace metal constituents of green petroleum coke were reported in API (2007). Review of the data indicates that the constituents of most interest and relevance to inhalation risk assessment are nickel and benzo (a) pyrene (B(a)P), which are regulated by AQD as carcinogens. The API (2007) report includes reported levels of 304.6, 95, 78, and 85 ppm nickel (in the 2003 micronized final sample, API sample #4-1-140, 1981 sample with 1981 analysis, and 1981 sample with 1984 analysis, respectively). MDEQ (2013) analytical results for a sample for the Detroit Bulk Storage site include 190 mg/kg nickel (dry weight; ppm). For comparison, statewide topsoil in MI contains a range of 5 to 47 ppm nickel (MDEQ, 2005). As noted above, the storage piles along the Detroit River have not been observed to be "dusty", and presumably the opacity is below 5% and the PM2.5 level is below the NAAQS of 12 ug/m^3. Using worst-case assumptions in order to address any concern that may exist for the inhalation of the components of the material, a petroleum coke dust level of 12 ug/m^3 with a nickel composition of 190 mg/kg would equate to 0.002 ug/m^3 nickel. This level is roughly half the AQD Initial Risk Screening Level (IRSL) for nickel of 0.0042 ug/m^3. In other words, under these worst-case assumptions, the nickel level would be associated with a lifetime incremental risk level of about 0.5 in one million. The API report

indicates that B(a)P was present in green petroleum coke samples from 13 to 440 ppm. Following the same worst-case assumptions as above, the highest level of 440 ppm B(a)P would be associated with a lifetime incremental cancer risk level of 10 in one million. These estimates do not raise particular concerns for the potential carcinogenicity of the material, in addition to the negative cancer bioassay results for petroleum coke as mentioned above.

In summary, there are substantial animal bioassay data available for evaluating the inhalation toxicity potential of green petroleum coke. The studies indicate that the substance has a low degree of toxicity. It did not cause carcinogenicity or systemic toxicity. The respiratory tract effects occurred at exposure levels that were much higher than the OELs for particulates not otherwise regulated. Lung clearance mechanisms for particulates can be overwhelmed at high concentrations; excessive lung dust burdens overwhelm macrophage-mediated particulate removal and lead to increasingly irreversible changes. "Dust overloading" results in increased dust material retention and chronic inflammation. This can occur with any material in fine particulate form that is insoluble and is persistently retained; it can occur in animal studies in the low mg/m^3 range. The petroleum coke repeated-dose animal studies at relatively high exposure levels resulted in macrophage accumulation (with test article deposits), pulmonary inflammation, and focal fibrosis, without systemic effects (EPA, 2011); these findings are consistent with dust overloading. These toxicity test findings, coupled with the low degree of "dusting" of the material and the low concern for trace metals and other constituents, support a conclusion that the storage piles do not pose a significant public health hazard for inhalation exposure.

References

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